

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 6,893,776 B2  
APPLICATION NO. : 09/986431  
DATED : May 17, 2005  
INVENTOR(S) : Yoshinori Naruoka, Junichi Toriyama and Masanao Terasaki

Page 1 of 4

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

**Please amend the second full paragraph in column 4 as follows:**

The present invention also relates to a positive active material for the non-aqueous electrolyte secondary battery comprising a lithium-nickel composite oxide represented by the compositional formula  $\text{Li}_a\text{Ni}_{1-b-c-d}\text{Co}_b\text{Mn}_c\text{M}_d\text{O}_2$  (in which M is at least one metal element selected from the group consisting of Al, Ti, W, Nb and Mo, the suffix a is not greater than 1.09 ( $a \leq 1.09$ ), the suffix b is from not smaller than 0.05 to not greater than 0.35 ( $0.05 \leq b \leq 0.35$ ), the suffix c is from not smaller than 0.15 to not greater than 0.35 ( $0.15 \leq c \leq 0.35$ ), and the suffix d is from greater than 0 to not greater than 0.35 ( ~~$0 \leq d \leq 0.35$~~ ) ( $0 < d \leq 0.35$ ), with the proviso that the sum of b, c and d is from not smaller than 0.25 to not greater than 0.55 ( $0.25 \leq b+c+d \leq 0.55$ )) having a hexagonal structure. When subjected to the X-ray diffractometry with the CuK.alpha. ray, the lithium-nickel composite oxide exhibits an intensity ratio  $R (= (I_{012} + I_{006}) / I_{101})$  of not greater than 0.50, R being the ratio of the sum of the diffraction peak intensity  $I_{012}$  on the 012 plane and the diffraction peak intensity  $I_{006}$  on the 006 plane to the diffraction peak intensity  $I_{101}$  on the 101 plane.

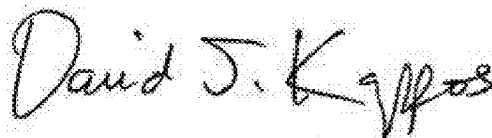
**Please amend the third full paragraph of column 4 as follows:**

By this constitution, the crystallinity of the positive active material represented by the compositional formula  $\text{Li}_a\text{Ni}_{1-b-c-d}\text{Co}_b\text{Mn}_c\text{M}_d\text{O}_2$  ~~an~~ can be kept high. At the same time, the adhesivity of the positive active material to the electrically conductive material and the binder in the positive electrode compound can be kept to inhibit the increase of internal resistance, making it possible to secure the excellent capacity density and cycle life performance.

**Please amend the last paragraph of column 6 bridging column 7 as follows:**

The organic solvent for the liquid electrolyte to be used in the non-aqueous electrolyte secondary battery of the invention is not specifically limited. Examples of the organic solvents

Signed and Sealed this  
Fifteenth Day of February, 2011



David J. Kappos  
Director of the United States Patent and Trademark Office

employable herein include ethers, ketones, lactones, ~~nitrites~~ nitriles, amines, amides, sulfur compounds, halogenated hydrocarbons, esters, carbonates, nitro compounds, phosphate compounds, and sulfolan-based hydrocarbons. Preferred among these organic solvents are ethers, ketones, esters, lactones, halogenated hydrocarbons, carbonates, and sulfolan-based compounds. Specific examples of these organic solvents include tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, anisole, monoglyme, 4-methyl-2-pentanone, ethyl acetate, methyl acetate, methyl propionate, ethyl propionate, 1,2-dichloroethane,  $\gamma$ -butyrolactone, dimethoxyethane, methyl formate, dimethyl carbonate, methyl ethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, vinylene carbonate, dimethylformamide, dimethyl sulfoxide, dimethylthioformamide, sulfolan, 3-methyl-sulfolan, trimethyl phosphate, triethyl phosphate, and mixture thereof. However, the present invention is not limited to these compounds. Preferred among these compounds are cyclic carbonates and cyclic esters. Even more desirable among these compounds are ethylene carbonate, propylene carbonate, methyl ethyl carbonate, and diethyl carbonate. These compounds may be used singly or in combination of two or more thereof.

**Please amend the first full paragraph of column 7 as follows:**

The electrolyte salt to be used in the non-aqueous electrolyte secondary battery of the invention is not specifically limited. In practice, however,  $\text{LiClO}_4$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{CF}_3\text{SO}_3\text{Li}$ ,  $\text{LiPF}_6$ ,  $\text{LiPF}_3$ ,  $(\text{C}_2\text{F}_5)_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  ~~$\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$~~   $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$ ,  $\text{LiI}$ ,  ~~$\text{LiAlCl}_4$~~   $\text{LiAlCl}_4$ , and mixture thereof may be used. Preferably, lithium salt such as  $\text{LiBF}_4$  and  $\text{LiPF}_6$  may be used singly or in admixture.

**Please amend the second full paragraph of column 7 as follows:**

As the electrolyte ~~for, the~~ for the present invention, a solid ionically-conductive polymer electrolyte may be used auxiliary. In this case, the structure of the non-aqueous electrolyte secondary battery may be a combination of a positive electrode, a negative electrode, a separator, an organic or inorganic solid electrolyte membrane as a separator, and the foregoing non-aqueous liquid electrolyte, or a combination of a positive electrode, a negative electrode, an organic or inorganic solid electrolyte membrane as a separator, and the aforementioned non-aqueous liquid electrolyte. A polymer electrolyte membrane made of polyethylene oxide, polyacrylonitrile, polyethylene glycol or modification product thereof has a light weight and flexibility and thus can be used as an electrode to be wound to advantage. Besides the polymer electrolyte, an inorganic solid electrolyte or a mixture of an organic polymer electrolyte and an inorganic solid electrolyte may be used.

**Please amend the last paragraph in column 7 bridging column 8 as follows:**

As the starting materials for the positive active material, a mixed carbonates represented by the compositional formula  ~~$\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{Mn}_c\text{Co}_2$~~   $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{Mn}_c\text{CO}_3$  (in which b and c vary from greater than 0 to smaller than 1 ( $0 < b < 1$ ;  $0 < c < 1$ )) and lithium hydroxide were mixed. The mixture was calcined at the temperature set forth in Table 1 in an oxygen atmosphere for 24 hours, and then ground to obtain a lithium-nickel composite oxide represented by the compositional formula  $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{Mn}_c\text{O}_2$  set forth in Table 1. As a result of analysis by the X-ray diffraction, it was confirmed that many of these composite oxides have a hexagonal structure. The composition of these

composite oxides were then quantitatively analyzed by the ICP emission spectroscopy. The results are set forth in terms of compositional formula of composite oxide in Table 1.

**Please amend the second full paragraph in column 8 as follows:**

~~All the positive active materials thus prepared exhibited a mean particle diameter of  $D_{50}$  of 11.0  $\mu\text{m}$  and a BET surface area of 0.60  $\text{m}^2/\text{g}$ . For the determination of the mean particle diameter  $D_{50}$ , the distribution of volume of particles was measured by the laser diffraction scattering method. The mean particle diameter corresponding to the volume of 50% was then determined. The BET surface area was measured by the  $\text{N}_2$  gas absorption method. (Preparation of positive electrode and test battery) To a positive electrode compound obtained by mixing 87% of the aforementioned positive active material, 5% by weight of acetylene black and 8% by weight of a polyvinylidene fluoride was added N-methyl-2-pyrrolidone to prepare a viscous material. A foamed aluminum having a porosity of 90% was filled with this viscous material, dried in vacuo at a temperature of 150°C. to cause N-methyl-2-pyrrolidone to evaporate thoroughly, and then pressure molded.~~

All the positive active materials thus prepared exhibited a mean particle diameter  $D_{50}$  of 11.0  $\mu\text{m}$  and a BET surface area of 0.60  $\text{m}^2/\text{g}$ . For the determination of the mean particle diameter  $D_{50}$ , the distribution of volume of particles was measured by the laser diffraction scattering method. The mean particle diameter  $D_{50}$  corresponding to the volume of 50% was then determined. The BET surface area was measured by the  $\text{N}_2$  gas absorption method.

(Preparation of positive electrode and test battery)

To a positive electrode compound obtained by mixing 87% of the aforementioned positive active material, 5% by weight of acetylene black and 8% by weight of a polyvinylidene fluoride was added N-methyl-2-pyrrolidone to prepare a viscous material. A foamed aluminum having a porosity of 90% was filled with this viscous material, dried in vacuo at a temperature of 150°C. to cause N-methyl-2-pyrrolidone to evaporate thoroughly, and then pressure-molded.

**Please amend the last full paragraph in column 8 as follows:**

~~The test battery was charged to 4.3 V (with respect to lithium metal) at a current of current of 1.0  $\text{mA}/\text{cm}^2$ , and then discharged to 3.0 V at a current of 1.0  $\text{mA}/\text{cm}^2$ . The discharge capacity at this point was then measured. Under these conditions, charge and discharge were then repeated. After 50 cycles of charge and discharge, the test battery was then measured for discharge capacity. The capacity retention was then calculated by dividing the discharge capacity by the initial discharge capacity.~~

In column 10, Table 2, please change the heading " $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{Mn}_c\text{O}_2$ " to --  $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{Mn}_c\text{O}_2$  --

In column 11, Table 3, please change the heading " $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{Mn}_c\text{O}_2$ " to --  $\text{Li}_a\text{Ni}_{1-b-c}\text{Co}_b\text{Mn}_c\text{O}_2$  --

Please amend the first full paragraph in column 13 as follows:

Subsequently,  $\text{Li}_{1.08}\text{Ni}_{0.53}\text{Co}_{0.14}\text{Mn}_{0.30}\text{Al}_{0.03}\text{O}_2$  was prepared as Example 26. The starting material of the positive active material was prepared by mixing  ~~$\text{Ni}_{0.55}\text{Co}_{0.15}\text{Mn}_{0.30}\text{Co}_3$~~   $\text{Ni}_{0.55}\text{Co}_{0.15}\text{Mn}_{0.30}\text{CO}_3$  with aluminum hydroxide  $\text{Al}(\text{OH})_3$  and lithium hydroxide  $\text{LiOH}$  in an amount of 0.03 mols and 1.1 mols, respectively, per mol of  ~~$\text{Ni}_{0.55}\text{Co}_{0.15}\text{Mn}_{0.30}\text{Co}_3$~~   $\text{Ni}_{0.55}\text{Co}_{0.15}\text{Mn}_{0.30}\text{CO}_3$ , and then calcining the mixture at a temperature of  $900^\circ\text{C}$ . in an oxygen atmosphere for 24 hours. The positive active material was then used to prepare a positive electrode and a battery in the same manner as in Example 1. The battery thus prepared was then measured for the diffraction peak intensity ratio, capacity density, discharge capacity retention, exotherm starting temperature and exotherm. As a result, the diffraction peak intensity ratio R was 0.458, the capacity density was 158 mAh/g, the discharge capacity retention was 91%, the exotherm starting temperature was  $253.0^\circ\text{C}$ ., and the exotherm was 357 J/g.